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# Testing of Oil Spill Treating Agents

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## ABSTRACT

This paper is a review of five types of chemical treatments for oil spills. Gelling agents change oil to a solid or semi-solid form, but are not widely used because of the large amount of agent required. Elastol, a recovery improvement agent, has been tested and proven to function well under a variety of conditions. A number of water-in-oil emulsion preventers and breakers have been proposed, but none is commercially-available. A demoussifier developed by Environment Canada has been recently tested and found to be effective. Surface washing agents contain surfactants and quantitative results on a number of these agents are presented.

Dispersants contain surfactants which are intended to break up oil into small droplets in the water column. No undisputed documentation exists to show that dispersants have been very effective in field situations, but analytical means to measure field effectiveness are poor. Laboratory effectiveness results are presented for a number of oils and dispersants. The main concern with treating agents is their effectiveness, and this is often dependent on molecular size and type. Oil has many molecular types and sizes, thus rendering treatment much less than totally effective.

## INTRODUCTION

A large number of chemical agents for treating oil spills have been promoted in the past 20 yr. During the seventeen years of the life of the Environmental Emergencies Technology Division, over 100 dispersants were tested for toxicity and/or effectiveness. Only eight products still remain on the accepted list and only approximately 15 products are still being produced. The compendium on oil spill treating agents prepared for the American Petroleum Institute in 1972 lists 69 dispersants and 43 beach cleanup agents, most of which are also dispersants.<sup>1</sup> Only two of these oil spill treating agents are current commercial products, but both are produced in different formulations. Over 50 biodegradation agents, including bacterial mixtures, enzymes or fertilizers, have been proposed and only five of these, all very recent inventions, remain on the market.

Ten sinking agents have been examined with none remaining commercial. The API compendium lists 18 sinking agents. None of the sinking agents remain on the market, primarily because they are banned in Canada, the United States and most other countries.

One recovery aid of the several proposed, Elastol, still remains commercially available. Ten emulsion breakers and preventers have been on the market. None are commercially available at this time. Over 100 surface washing agents have been sold in the North American market. Twelve of these agents are still commercially available.

A number of agents which have been sold for various purposes, but

do not fit into the above categories, include those that help trace or detect an oil, those which are combinations of the categories described above, and those very vague items that are claimed to make oil disappear, become non-toxic, etc. It is estimated that more than 100 of this category of agent have been offered at one time or another on the North American market. The total number of agents proposed world wide is estimated to be 600, of which only about 200 were ever tested in laboratory or field, even in a limited way. It is also estimated that only 35 agents actually are commercially available at this time. The bustle of activity in this field has left the potential buyer confused and sceptical of treating agents.

Effectiveness will remain the major problem with most treating agents. Effectiveness is generally a function of molecular size and type. Crude and refined oil products have a wide range of molecular sizes and composition including whole categories of materials like asphaltenes, alkanes, aromatics and resins. What is often effective for a small asphaltene is ineffective on the large asphaltene. What is effective on an aromatic compound may not be effective on a polar compound. Additionally, the composition of crude oils varies widely. This leaves little scope for a universally-applicable and effective spill control chemical.

Testing of spill treating agents has involved two facets at Environment Canada: the first is testing for toxicity and other forms of environmental acceptability, and the second is effectiveness testing. A number of projects have been initiated to develop tests and to complete testing of most spill treating agents currently being sold.

## GELLING OR SOLIDIFICATION AGENTS

Gelling agents are those agents which change oil from a liquid to a solid. Also known as solidification agents, these agents often consist of polymerization catalysts and cross-linking agents. Agents which are actually sorbents are not considered to be gelling agents. Three gelling agents were tested by Environment Canada and others in recent years:

- The BP (British Petroleum) product which consisted of deodorized kerosene and a cross linking agent
- A Japanese product consisting of an amine which forms a polymer
- The solidification agent proposed by Professor Bannister of the University of Lowell, an agent which used liquefied carbon dioxide and an activating agent.

During tests conducted in the laboratory, all three agents functioned, but required large amounts of agent to effectively solidify the oil. Under some situations, the oil became a semi-solid which would not aid in recovery. The BP agent worked better than the other agents and was tested in larger scale by the Canadian Coast Guard and the Canadian oil industry. In these large scale tests, even more agent was required to solidify the oil up to 40% of the actual volume of the oil itself.

This is double the laboratory requirement. Both requirements were deemed to be far in excess of what was actually practical in the event of a real spill. Because of the large amount of agent required, gelling agents have not been historically used nor stocked for use by spill responders.

A standard test was developed to assess new solidifiers. The test consists of adding solidifier to an oil while being continuously stirred until the oil is solid. The test is repeatable within 5%, even with different laboratory personnel. Results of testing some solidifiers are given in Table 1. Values are given as the weight percent required to solidify an oil completely. Elastol is an oil recovery enhancer, not a solidifier, but was included for comparison.

Table 1  
Solidifier Test Results

Product Name	Percentage To Solidify
RAWFLEX	16
Elastol	26 (note, this product is a recovery enhancer, not a solidifier)
Oil Bond 100	33
Oil Sponge	36
Petro Lock	44
Molten Wax	109
Powdered Wax	278

## RECOVERY AIDS AND DEMOUSSIFIERS

A number of agents have been sold throughout the years to assist in the recovery of spilled oil. None has been widely known or promoted except for Elastol. Earlier agents were neither well tested nor were they sophisticated. One product, shredded peat moss, was claimed to improve the recovery efficiency of sorbent-surface devices. None of these earlier agents offered enough promise to warrant extensive testing.

A number of agents were also available to break or prevent emulsions. Most agents were hydrophillic surfactants, that is surfactants with a strong tendency to make oil-in-water emulsions. Such surfactants have the ability to reverse the water-in-oil emulsion to two separate phases. The problem with a hydrophillic surfactant is that it is more soluble in water than in oil and will quickly leave the system if there is sufficient water. Obviously, such products cannot be successfully used on open water. Some recent products avoided this problem by using a less water-soluble surfactant and accepting the resulting decrease in effectiveness. One recent product, "Demoussifier", was developed by Environment Canada and does not use surfactant in the normal sense of the word. This product does not suffer the limitations noted above.

Two commercial products, Exxon Breaxit and a Shell product, LA 1834, and a surfactant, sodium dioctyl sulfosuccinate were evaluated in one study.<sup>2</sup> All three products functioned in a limited way, but only the Shell product prevented the formation of emulsions over a wide range of oils and conditions. The Shell product and the Exxon product are not commercially available, but have been obtainable in small quantities for testing.

The United States Minerals Management Service and Environment Canada joined forces to evaluate two new and promising treating agents, Elastol, a recovery-enhancement agent, and Demoussifier, an emulsion breaker and preventer. Results of the extensive testing on these products have been widely published.<sup>3,4,5,6,7,8</sup> Elastol is a non-toxic powder and renders oil visco-elastic making it adhesive to oil spill recovery surfaces. Demoussifier is a mixture of long-chain polymers which again have no measurable toxicity to humans or aquatic life. This product was developed at Environment Canada's River Road Environmental Technology Centre and functions both to break emulsions and prevent their formation. The laboratory work on Elastol involved several different tests.

The effect of Elastol on a suite of different oils was determined by measuring the time to initiate change and the degree of elasticity formed. All oils display viscoelastic properties when treated with doses of 600 to 6000 ppm Elastol. In general, more viscous oils tend to attain a higher degree of elasticity than non-viscous oils, but do so over a longer period of time.

Under low mixing energy conditions, oils exhibit some degree of elasticity within 15 min of Elastol application. A high degree of elasticity is not displayed until 1 hr after treatment. Less viscous oils take less time to reach maximum elasticity and viscous oils take more time. At higher mixing energies, maximum elasticity is reached in much less time. Elastol causes a minor reduction in the rate of oil evaporation, but not significant enough to reduce its flash point. The addition of Elastol either has no effect or an inhibiting effect on the formation of water-in-oil emulsions. Testing with the Demoussifier showed the Elastol has no effect on its operation and that both products could be used together.

Both Elastol and Demoussifier were tested on a large scale using the Esso test tank in Calgary, Alberta. Funding for this part of the program was provided by the U.S. Minerals Management Service, Environment Canada and Esso Resources. In the large scale tests, two slicks were put out simultaneously in parallel booms. Using two slicks permitted the simultaneous testing of a control and a treated slick under identical conditions. The first 2 days were devoted to the testing of Demoussifier. Demoussifier prevented the formation of water-in-oil emulsions on both slicks and did so at treatment ratios as low as 1:2000 (500 ppm). Elastol was tested on the final 2 days. In the first of these tests, Elastol was added to a test crude oil at 4000 ppm and the test slick was released several hours later when the oil was highly elastic. Although not thick enough to burn, the high elasticity increased the recovery rate by a rotating disk skimmer. On the fourth day of testing, crude oil was treated with 2000 ppm of Elastol and recovered with a skimmer. The recovery rate was again high and exceeded the capacity of the skimmer's pump to remove it. The tank-scale tests showed that there were no scaling effects for either the Elastol or the Demoussifier. Both products worked well for the intended purpose. Elastol increased the visco-elasticity of the oil and greatly increased the skimmer recovery rate. Elastol, however, did not reduce the spreading or increase the thickness of the slick sufficiently to allow in situ burning. Demoussifier prevented the formation of water-in-oil emulsions and also broke emulsion already formed. Although Demoussifier causes the oil to be less adhesive and lowers the recovery rate of skimmers, the two products can be applied together to achieve positive results.

The two products were then tested on a large scale offshore. The sponsors of this test included U.S. Minerals Management Service, Environment Canada, Esso Resources and the Canadian Coast Guard. The field trial was conducted 50 mi off shore of Nova Scotia. Five slicks of 5-bbl size each were laid for each of the products, and each product was tested both pre-mixed and by application-at-sea to confirm that application effects were not a factor.

The Demoussifier trials were performed by laying down a five-barrel oil slick, treating it with the product at the specified ratio, taking samples at subsequent intervals and measuring the water content and the viscosity. One slick was left untreated and then treated at the 240 min interval to test Demoussifier's ability to break emulsion at sea. A large reduction in viscosity (105,000 to 22,600 cSt) occurred over the 30 min period between samples, showing that the product worked well to break the emulsion. The product continued to work well over the 5 hr test period to prevent the formation of emulsions.

The Elastol tests were performed in an analogous manner to those for Demoussifier, with one control slick laid and one slick being pretreated to test the effect of at-sea treatment. The slicks were sampled periodically, and both viscosity and elasticity were measured immediately on board ship. The elasticity of the treated slicks was significantly higher than that of the untreated slicks and corresponded to that experienced in the laboratory. In fact, it actually exceeded laboratory results at higher doses. This unexpected result is probably due to the better mixing achieved in the field situation.

## SURFACE WASHING AGENTS

The most common and most suggested treating agents are those containing surfactants as the major ingredient. These agents have been divided into two groups, dispersants and surface washing agents. Dispersants are those agents which have approximately the same solubility in water and oil and will cause the oil to be dispersed into the water in fine droplets. Surface washing agents are those agents which remove oil from solid surfaces such as beaches by a mechanism known as detergency. The mechanisms of dispersancy and detergency are quite different, and testing has found that a product that is a good surface washing agent is a poor dispersant and vice versa.

A test for surface washing agents was developed by Environment Canada and a number of commercial products have been tested using this protocol.<sup>9</sup> The test measures how much oil is removed from a standard test surface when the surface washing agent is allowed to soak into the oil and then water is used to rinse off the oil. Table 2 shows the results of these tests with a seawater rinse and the results of an aquatic toxicity test (lethal concentration to Rainbow Trout over 4 days in mg/L, larger values indicate less toxicity) and a dispersant effectiveness test (swirling flask test, values represent percent oil put into the water column) for the same products. This latter data point was included to show the opposite nature of dispersant and surface-washing effectiveness. Some products display neither property. Only one product tested, Corexit 9580 is relatively effective as a surface washing agent and has low toxicity.

Table 2  
Surface Washing Agent Test Results

Agent	Percent Oil Removed	Toxicity	Dispersant Effectiveness
Corexit 9580	42	>5600	0
Citrikleen XPC	36	34	2
Corexit 7664	27	850	2
BP 1100 WD	21	120	6
Palmolive dish soap	16	13	9
Breaker 4	13	340	0
Nukomis 3	13	110	0
Sunlight dish soap	12	13	9
Citrikleen 1855	12	55	0
Con-Lei	12	70	0
Mr. Clean	6	30	0
Corexit CRX-8	5	20	48
Corexit 9527	3	108	41
Biosolve	2	9	0
Leatoil	1	51	0
Energizer 700	1	50	56

## DISPERSANTS

Dispersants comprise the largest class of oil spill treating agents and have perhaps generated the greatest number of studies and discussion since the birth of the oil spill countermeasures industry 20 yr ago with the TORREY CANYON incident. Discussion is still as lively today as then and there still exists a polarization between dispersant proponents and opponents. Little has changed in the way of documentation. There is still no undisputed documentation on large-scale experiments or use to show whether or not dispersants are effective. Similarly, no large scale biological experiments have convinced all environmentalists that the use of dispersants is safe in all conditions, although the evidence is becoming increasingly clear that dispersants cause little ecological damage above that by untreated oil and that they could in fact minimize ecological damage if they were effective.<sup>10,11</sup>

Field tests of oil spill dispersants have not been successful. Over the past 12 yr, 107 test spills have been laid out to test the effectiveness of oil spill dispersants.<sup>12</sup> The results of these tests are summarized in

Table 3. A number of smaller tests or other tests which were not documented have taken place but are not included here. Of the 107 slicks documented, 23 were controls used to establish a comparison. Percentage effectiveness is reported in 25 spills and the average for these is 30%. Effectiveness values range from 0 to 100%. Most experimenters have not assigned effectiveness values because, as will be demonstrated in more depth later, effectiveness values are hard to compute.

Table 3  
Dispersant Effectiveness Results

Oil	Percent effectiveness with Dispersant			
	Corexit 9527	Corexit CRX-8	Energizer 700	Basic Slickgone
Alberta	33	45	51	24
Bunker C	1	2	2	1
California heavy	1	1	1	1
Hibernia	6	6	10	14
Hibernia weathered	4	3	8	7
Lago Medio	5	5	13	15
Prudhoe Bay	7	7	10	14
Prudhoe Bay weathered	4	4	8	10
South Louisiana	31	36	46	42
Used Motor oil	33	31	36	29

The trends that are notable in these data are that weathered oils disperse poorly, and heavy oils are very difficult to disperse.

The test results show clearly that dispersants are not highly effective, even under highly controlled experimental situations. Of greater concern than this is the methodology used to estimate effectiveness. Some experimenters simply estimated effectiveness, but most based their measure on integrations of water column concentrations relative to surface slick dimensions. This technique is not a correct means to perform the measure because the underwater concentrations have little positional relationship to the surface slick. Underwater dynamics of the ocean are very different than surface dynamics. Extreme cases of the positional variances between surface and sub-surface slicks have been illustrated by Brown and Goodman in controlled tank testing.<sup>13</sup> Their work has shown that the underwater plumes move in highly random fashions with respect to the surface slick and even two trials conducted on the same day and in the same tank location will not have similar movement patterns. Furthermore, all of the experimenters who used underwater concentrations to estimate field effectiveness also used the method of dividing the water into different compartments and averaging concentrations. Mathematically this approach is not appropriate and can result in effectiveness values that are much larger and range from two to 10 times greater than the actual values. Because of these factors, underwater estimates of oil spill dispersant effectiveness are highly inaccurate and misleading. Surface measures are also inadequate at this time but may be possible with the development of new remote sensors.<sup>14</sup>

In summary, field trials of dispersant effectiveness have not shown any quantitative or qualitative proof of high (> 50%) dispersant effectiveness. Analytical means do not currently exist to accurately quantify dispersant effectiveness at field trial situations.

A number of laboratory studies have been performed to compare the test results from different apparatus and procedures. A review of these results shows that there is poor correlation in effectiveness results between the various test methods.<sup>15</sup> A recent study by the present author has shown that lack of correlation is primarily a function of settling time allowed between the time that the energy is no longer applied and the time that the water sample is taken from the apparatus.<sup>16</sup> Another important experimental factor that determines effectiveness is the oil-to-water ratio in the apparatus. When these two parameters are adjusted to be the same and to larger values, test results from most apparatus are similar. Results from more energetic dispersant effectiveness tests

are higher but when corrected for natural dispersion, these results are nearly identical to those from less energetic apparatus. Given that essentially identical results can now be obtained from virtually any laboratory tests, a simple, repeatable and fast test can be chosen to make determinations of the dispersant effectiveness. One test developed by Environment Canada, called the "swirling flask" test, meets these criteria and has been used to test many combinations of oil/dispersant effectiveness (16). Some of these test results are given in Table 3.

The trends that are notable in these data are that weathered oils disperse poorly, and heavy oils are very difficult to disperse.

## CONCLUSION

Testing of spill treating agents shows that clear differences exist in their efficiencies and effectiveness with different oils. The testing of effectiveness along with toxicity is an important screening tool for selecting treating agents.

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